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Mercury and methylmercury in water and sediment of the Sacramento River Basin, California

Joseph Domagalski*

US Geological Survey, Water Resources Division, Placer Hall, 6000 J Street, Sacramento, CA 95819, USA

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Abstract

Mercury (Hg) and methylmercury (CH_3Hg^+) concentrations in streambed sediment and water were determined at 27 locations throughout the Sacramento River Basin, CA. Mercury in sediment was elevated at locations downstream of either Hg mining or Au mining activities where Hg was used in the recovery of Au. Methylmercury in sediment was highest (2.84 ng/g) at a location with the greatest wetland land cover, in spite of lower total Hg at that site relative to other river sites. Mercury in unfiltered water was measured at 4 locations on the Sacramento River and at tributaries draining the mining regions, as well as agricultural regions. The highest levels of Hg in unfiltered water (2248 ng/l) were measured at a site downstream of a historic Hg mining area, and the highest levels at all sites were measured in samples collected during high streamflow when the levels of suspended sediment were also elevated. Mercury in unfiltered water exceeded the current federal and state recommended criterion for protection of aquatic life (50 ng/l as total Hg in unfiltered water) only during high streamflow conditions. The highest loading of Hg to the San Francisco Bay system was attributed to sources within the Cache Creek watershed, which are downstream of historic Hg mines, and to an unknown source or sources to the mainstem of the Sacramento River upstream of historic Au mining regions. That unknown source is possibly associated with a volcanic deposit. Methylmercury concentrations also were dependent on season and hydrologic conditions. The highest levels (1.98 ng/l) in the Sacramento River, during the period of study, were measured during a major flood event. The reactivity of Hg in unfiltered water was assessed by measuring the amount available for reaction by a strong reducing agent. Although most Hg was found to be nonreactive, the highest reactivity (7.8% of the total Hg in water) was measured in the sample collected from the same site with high CH_3Hg^+ in sediment, and during the time of year when that site was under continual flooded conditions. Although Hg concentrations in water downstream of the Hg mining operations were measured as high as 2248 ng/l during stormwater runoff events, the transported Hg was found to have a low potential for geochemical transformations, as indicated by the low reactivity to the reducing agent (0.0001% of the total), probably because most of the Hg in the unfiltered water sample was in the mercury sulfide form. Published by Elsevier Science Ltd.

1. Introduction

Mercury is currently one of the most serious contaminants in water, sediment, and fish tissue at many locations in northern California, especially within the Sacramento River Basin (Fig. 1) and downstream in the San Francisco Bay (Rasmussen and Blethrow, 1990).

Advisories on the consumption of certain species of fish have been posted for the San Francisco Bay region of California (San Francisco Regional Water Quality Control Board, 1995) and elsewhere. Elevated levels of Hg in fish are known to cause neurotoxic responses in humans, and those effects are thought to be most serious to developing fetuses (World Health Organization, 1990). Although all areas of the world receive atmospheric input of Hg to aquatic systems, the most important sources of Hg to the environment in California are from historic Hg mining operations, the use

* Tel.: +1-916-278-3077; fax: +1-916-278-3071.

E-mail address: joed@usgs.gov (J. Domagalski).

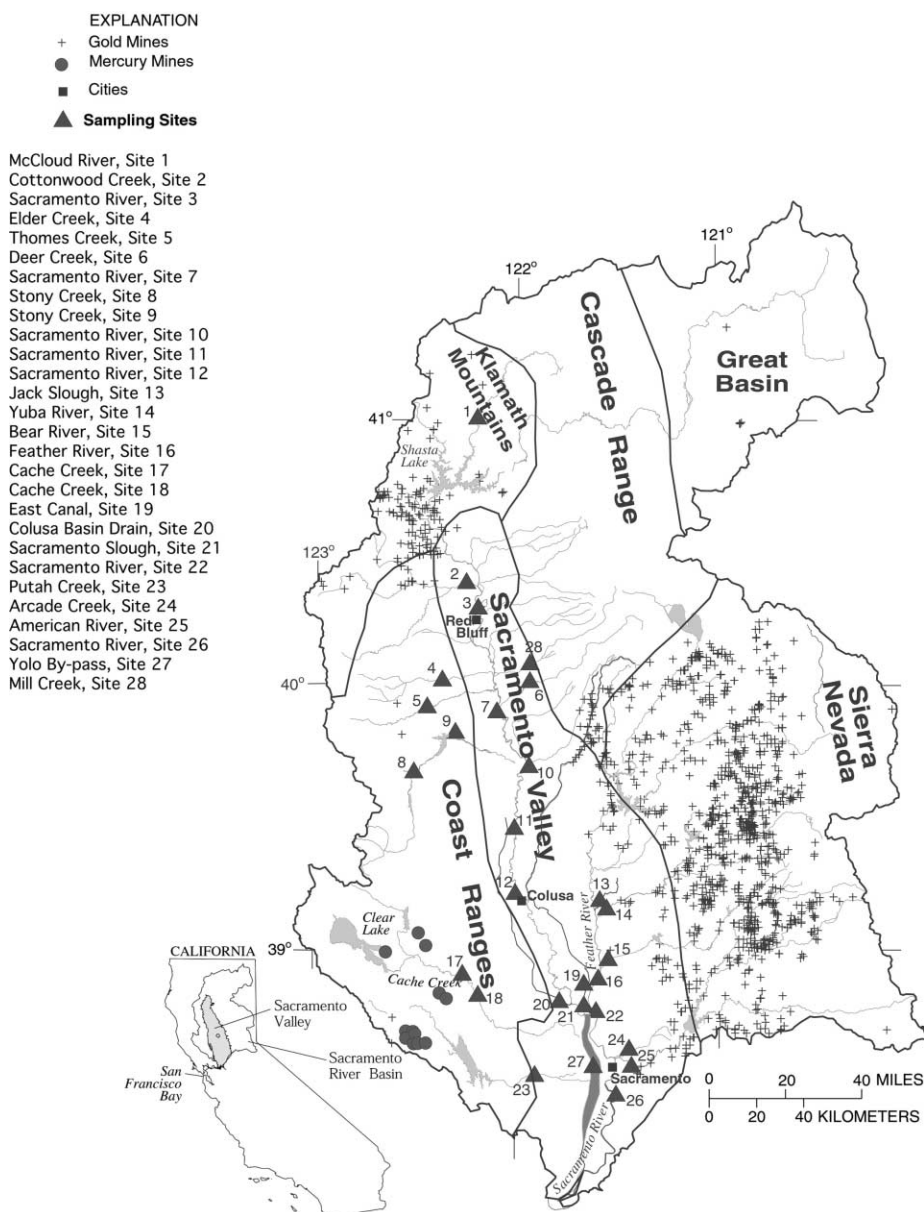


Fig. 1. Sacramento River Basin, physiographic provinces, locations of Hg mines and gold mines, locations of sampling sites.

of Hg for the processing of Au from either placer deposits or primary ore deposits, and natural geological features. Mercury was mined in California at several locations within the Coast Ranges, in the form of mercury sulfide (HgS) (Fig. 1), and then transported to the Sierra Nevada Au mining regions (as elemental Hg) where it was used in Au recovery operations (Fig. 1) (Bradley, 1918). The forms of Hg residues in the California environment are therefore complex and include sulfide, elemental, and other forms attached to sedimentary particles, or within the tissue of aquatic organisms (Domagalski, 1998).

Methylmercury is the form of Hg most typically detected in tissue. Before Hg can bioaccumulate in fish, the inorganic form must be converted to the organic form, CH_3Hg^+ (Zilloux et al., 1993). The processes that result in a net production of CH_3Hg^+ in a given ecosystem are incompletely understood, but 1 step is known to be associated with bacteria in anoxic sedimentary environments, especially bacteria that are associated with the chemical reduction of SO_4^{2-} to S^{2-} (Gilmour et al, 1992, Compeau and Bartha, 1985). A large scale effort to restore wetland ecosystems of the San Francisco Bay region of California will require that consideration be

given to the consequences of permanently flooding currently dry land containing Hg residue. This flooding may result in localized increased rates of Hg methylation and accumulation in fish, thereby resulting in a human health problem from fish consumption. Wetlands can potentially be important for the formation of CH_3Hg^+ (Zilloux et al., 1993; Rudd, 1995). It is also necessary to know how much Hg and CH_3Hg^+ would be transported by the major rivers to these sites of wetland restoration.

To address these questions regarding Hg occurrence in the Sacramento River Basin, a study was initiated in 1995 (Domagalski, 1998) to evaluate the levels of Hg in sediment and water, determine the loadings of Hg to the San Francisco Bay, assess the reactivity of the transported Hg, and to assess the levels of CH_3Hg^+ at select locations in the Sacramento River Basin. A previous report (Domagalski, 1998) discussed the preliminary results from the first year of that study and included information on Hg concentrations in river sediment at select locations of the Sacramento River Basin, Hg loads to the San Francisco Bay following an extreme flood, starting 1 January 1997, that affected a large part of the Sacramento River Basin, and included the first reported data on CH_3Hg^+ in water of this river system. Continuation of the study after the first year allowed for the sampling of water and sediment following this extreme high river flow event and to allow for the study of Hg occurrence in water during a subsequent wet-weather season with associated high river flows caused by the El Niño weather phenomenon, and a final year of sampling when rainfall amounts and river flow were much lower, thereby allowing for a comparison of Hg loadings during variable climatic and streamflow patterns. The term El Niño refers to an ocean–atmosphere phenomenon during which wind and ocean current in the equatorial Pacific result in warmer than normal water along the North and South American Pacific coasts. El Niño winters frequently bring higher than normal precipitation in northern California because of a southward shift of the jet stream. Sites were selected for stormwater runoff studies during the second year of the study that were not evaluated during the first. The continuation of the study included investigation of Hg reactivity under both low flow and high flow conditions, thereby providing some indication of the availability of this Hg to undergo biogeochemical transformations in the various rivers of this basin. Methylmercury in sediment was also sampled in the second year of the study. Taken as a whole this study provides the most detailed information available on Hg and CH_3Hg^+ concentrations and loads under variable climatic conditions available for the Sacramento River Basin thereby providing critical baseline information for management decisions currently under consideration for ecosystem restoration of the San Francisco Bay system.

2. Description of study area

The Sacramento River Basin covers approximately 70,000 km² in northern California (Fig. 1). It is the largest river in California and has an average streamflow of over 650 m³/s and an annual runoff of 27,600 hm³. The Coast Ranges and Sierra Nevada (Fig. 1) regions were considered to be most significant for Hg transport, although other regions also may contribute Hg to the Sacramento River including portions of the Cascade Range and the Klamath Mountains. Most of the Hg mines of the Sacramento River Basin are located near Clear Lake (Fig. 1). The Clear Lake Cenozoic hydrothermal Hg deposits are the northern part of a group of similar deposits associated with volcanism and the migration of a transform fault system (Rytuba, 1996). The locations of Sierra Nevada Au mines are also shown in Fig. 1. Clark (1966) has described the Au deposits of the Sierra Nevada. More information on these deposits has been provided previously (Domagalski, 1998).

The average annual precipitation for the Sacramento River Basin is 91.4 cm, most of which is from rain or snow during the months of November through March. Agriculture is one of the major land uses of the low-lying Sacramento Valley. Because of poorly drained or relatively impermeable soils in much of the valley, rice cultivation is a major agricultural land use.

3. Study design and selection of sampling sites

All sampling sites for the study are shown in Fig. 1 and listed in Table 1. Details of sampling site selection for water and sediment have been described previously (Domagalski, 1998). Briefly, Hg in unfiltered water was measured at 12 sites from February 1996 to April 1998 on a monthly basis to assess the variability in concentrations throughout the year, and at select sites following precipitation events, to determine the concentrations of Hg in stormwater runoff and to determine Hg mass loadings. The sites were selected to bracket the range of river conditions on the mainstem of the Sacramento River below Shasta Lake to the mouth of the river, and to assess the loading of Hg to the Sacramento River from various source areas. Mercury in stormwater runoff in the mainstem of the Sacramento River investigated during the first year of this study was previously reported on (Domagalski, 1998). The Cache Creek watershed, which has several abandoned Hg mines, and the Yolo Bypass, which carries stormwater runoff from a large portion of the entire basin were given priority for stormwater sampling during the second year of the study. Mercury in unfiltered water continued to be monitored at 3 locations after May 1998 to obtain information on the loadings of Hg to the San Francisco Bay. One site, Mill Creek (site 28, Fig. 1) was sampled in the winter of

Table 1
Sampling sites, and types of samples collected

Site number	Site name	Sediment collection 1995	Sediment collection 1997	Sediment collection 1998	Mercury in water	Methylmercury in water
1	McCloud River Below Ladybug Creek near McCloud	X				
2	Cottonwood Creek near Cottonwood, CA	X	X	X		
3	Sacramento River above Bend Bridge near Red Bluff	X	X		X	
4	Elder Creek below Government Gulch near Tehema		X			
5	Thomes Creek at Flournoy		X			
6	Deer Creek near Vina	X				
7	Sacramento River at Woodson Bridge		X			
8	Stony Creek above Black Butte Reservoir near Chrome		X			
9	Stony Creek below Black Butte Dam near Orland	X				
10	Sacramento River below Big Chico Creek near Chico		X			
11	Sacramento River at Butte City		X			
12	Sacramento River at Colusa	X	X		X	X
13	Jack Slough at Highway 70 near Marysville	X				
14	Yuba River at Marysville	X	X		X	
15	Bear River at Highway 70 near Rio Oso	X	X	X		
16	Feather River near Nicolaus	X	X		X	
17	Cache Creek at Rumsey				X	
18	Cache Creek at Guinda	X	X			
19	East Canal at Kirkville Road near Nicolaus	X				
20	Colusa Basin Drain at Road 99E near Knights Landing	X	X	X	X	X
21	Sacramento Slough near Knights Landing		X	X	X	X
22	Sacramento River at Verona	X	X		X	X
23	Putah Creek below Road 94A near Davis			X		
24	Arcade Creek near Del Paso Heights	X			X	
25	American River at Sacramento	X	X		X	
26	Sacramento River at Freeport	X	X		X	X
27	Yolo Bypass at Interstate 80 near West Sacramento		X		X	
28	Mill Creek at Los Molinos ^a				X	

^a Sampled only in 2000.

1999–2000 to determine Hg and CH_3Hg^+ loads during stormwater runoff conditions. Mill Creek drains the Lassen volcanic area and this site was sampled in order to determine the extent of one geologic source of Hg and CH_3Hg^+ to the Sacramento River from this volcanic system. Methylmercury in water was sampled at 5 locations from February 1996 to April 1998 to determine concentrations in the Sacramento River and to determine the effects of agricultural land use on CH_3Hg^+ concentrations. Rice production is a major agricultural land use of the Sacramento Valley. Rice production involves flooding a field thereby creating a seasonal wetland. The drainage from these fields was sampled for CH_3Hg^+ to determine if the CH_3Hg^+

concentrations in agricultural drainage exceeds that of the major rivers and contributes significantly to CH_3Hg^+ mass loading of the Sacramento River. Sites on the Sacramento River above and below the discharge of agricultural drainage were sampled for CH_3Hg^+ . On 2 occasions, the amount of reactive Hg in river water was assessed by determining the percentage capable of being reduced to elemental Hg by SnCl_2 . Reactive Hg was assessed at all 12 streamwater sampling sites. SnCl_2 will react with Hg in the Hg^{2+} form, unless that form of Hg is tightly bound to suspended sediment particles or organic C. Reactive Hg provides some information on the availability of Hg for biogeochemical reactions at the time of sampling.

Sampling sites for streambed sediment were initially chosen to provide information on the spatial distribution of Hg at representative sites in the basin. A total of 17 sites on the Sacramento River and tributaries were selected for sampling of Hg in streambed sediment. That sampling took place during the fall of 1995 when river flows were low. The sites, selected to be representative of a range of conditions throughout the basin, were located in downstream areas so that the integrated effects of streambed sediment chemistry of whole basins could be adequately assessed. A second sampling of streambed sediment took place during the spring and summer of 1997. A major flood, which occurred on 1 January 1997, affected the lower Sacramento River, and high river flow was recorded over much of the basin. The 1997 sampling of streambed sediment had 2 purposes. The first was to determine if the extreme river flows associated with the flooding had any effect on the distribution of Hg in river sediment. The second purpose was to sample additional sites to obtain Hg in sediment data not previously available. It was anticipated that Hg data from these additional sites might help to identify other major sources of Hg to the Sacramento River. The first year of the study documented that unknown sources contribute substantial loads of Hg to the mainstem of the Sacramento River. Therefore, the additional sites were chosen to help determine the locations of those sources. A total of 19 sites were sampled in 1997 for Hg concentrations in streambed sediments. The final sampling was completed during the summer of 1998 as part of a national sampling program for Hg and CH_3Hg^+ in sediment. Although only 5 sites were sampled during 1998, CH_3Hg^+ was included in the sampling design. Site selection was based on the results of previous sediment sampling.

4. Methodology

Samples for Hg in streambed sediment were collected by selecting a 100-m reach of river and collecting material from sediment deposition zones. The composite sample was collected with a Teflon spoon and placed in an acid-cleaned glass container. After thorough mixing, the sample was sieved through a 63- μm screen and placed in an acid-cleaned plastic jar. Sample collection for CH_3Hg^+ in sediment was similar, but the sediment was not sieved. The sample for CH_3Hg^+ in streambed sediment was stored in a Teflon jar and frozen after collection. Samples for Hg and CH_3Hg^+ in unfiltered water were collected using dedicated equipment and clean techniques to minimize contamination; Teflon sampling equipment and bottles were used. Three-liter Teflon bottles, equipped with Teflon nozzles for the collection of isokinetic samples, were used for sample collection. Prior to sampling, the Teflon equipment was soaked in

an acid bath containing 10% HCl at a temperature of 65°C for 48 hours. The equipment and bottles were rinsed with clean water, and all bottles were filled with 1% HCl. The bottles were capped tightly with a wrench and double-wrapped in plastic bags for transport. At the field site, the bottles were rinsed 3 times with native water, filled with the sample, preserved with approximately 10 mL of 50% HCl, recapped tightly with a wrench and double-wrapped in plastic bags. The procedure for collecting CH_3Hg^+ in unfiltered water samples was similar, except that the preservation method was freezing of the sample. At all sites, a depth-integrated sample was collected at a single point of the river, usually near the center of the channel or that part of the stream with the greatest discharge. At all streamwater sampling sites, samples were also collected for dissolved and particulate organic C, major cations and anions, nutrients, pH, alkalinity, conductivity, suspended sediments, temperature, and dissolved O_2 .

Sediment samples were analyzed for Hg after acid digestion by cold-vapor/atomic absorption spectrometry (Arbogast, 1990). The detection limit was 0.02 $\mu\text{g/g}$. The overall precision of that method was determined by analyzing a standard shale 10 times and achieving a relative standard deviation of 5.8. Analyses of Hg in unfiltered water samples were completed according to the US Environmental Protection Agency (EPA) Method 1631 (1996). That method uses BrCl oxidation, two-stage Au amalgamation, and cold-vapor/atomic fluorescence detection; the method achieves a detection limit of 0.04 ng/l. Precision of the method is at least 10% as determined by duplicate analysis of all laboratory samples. Spike recoveries are between 90% and 110%. Analyses of CH_3Hg^+ in water were completed according to EPA Method 1630 (US EPA, 1997). According to that method, CH_3Hg^+ is distilled and ethylated. The distillation process separates CH_3Hg^+ from interfering substances, such as dissolved organic C. The detection limit was 0.025 ng/l. The specified precision is 20%, and recovery of spiked samples averages 80–120%. A similar method was used for CH_3Hg^+ in sediment.

Samples for reactive Hg in unfiltered water (~1700 ml) were immediately placed after collection in a sealed Teflon container, to which 5 ml of a 20% solution of SnCl_2 were added. Nitrogen was bubbled through the sample for 1 h, and the volatile elemental Hg was collected in a tube containing Au beads. The Hg was then analyzed in a similar manner as that described for Hg in unfiltered water.

Field-level quality assurance for sediment analyses consisted of the collection of triplicate samples to check for variability in collection or analytical procedures. Those samples showed that the variability caused for sampling or analytical error was <5%. Replicate samples for total Hg in unfiltered water were collected each

month at 3 randomly selected sites, and replicate samples for CH_3Hg^+ in unfiltered water were collected at 1 randomly selected site per month. The replicates were discrete samples collected sequentially. Therefore, 25% of all samples of Hg in unfiltered water were replicate samples, and 20% of CH_3Hg^+ in unfiltered water samples were replicates. The average replicate difference for the analysis of Hg in unfiltered water was 12.1%. Because CH_3Hg^+ concentrations in unfiltered water are much lower than those for total Hg, higher relative differences among replicate samples result. The average replicate difference for CH_3Hg^+ analyses was 41.7%. Blank samples of unfiltered clean laboratory water also were submitted for total Hg analysis. The clean water was placed in the sampling equipment. Results of blank analyses showed that Hg in unfiltered water concentrations were 10 times less than the lowest Hg concentra-

tions in samples collected in the Sacramento River Basin, while the unfiltered CH_3Hg^+ blanks were less than the detection limit.

5. Results

5.1. Mercury in sediment

Mercury concentrations above the worldwide average crustal abundance ($0.067 \mu\text{g/g}$; Cox, 1989) were measured at most sites for this study (Fig. 2). There are no historical data on the concentrations of Hg in streambed sediment before the advent of mining in California. Because Hg was used extensively in the Sierra Nevada Au mining region, it is reasonable to assume that the Hg concentrations would be lower than those measured

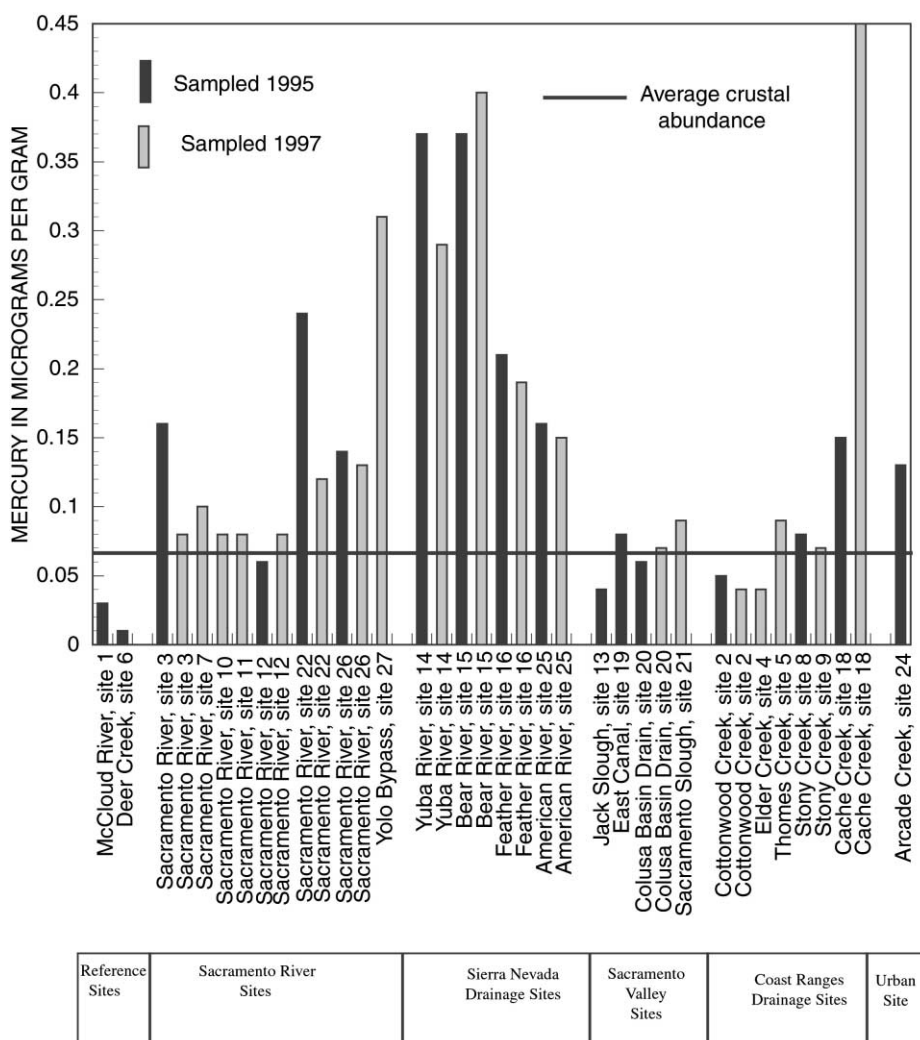


Fig. 2. Concentrations of Hg in streambed sediment.

today at some locations. Since premining sediment concentrations are not known for the Sacramento River Basin and insufficient data are available for a statistical comparison of these sites with other locations in this basin, including non-mineralized areas, average crustal abundance is used to compare recently measured concentrations. Concentrations above average crustal abundance do not necessarily imply contamination. Reference sites were selected in areas of no known Hg geological deposits or areas of anthropogenic use. Higher amounts of Hg (approximately 0.24 $\mu\text{g/g}$ and above) tended to be measured at sites downstream of the Sierra Nevada Au country, or below the Clear Lake Hg mining region. The flood control channel of the Sacramento River — the Yolo Bypass — also has elevated Hg concentrations (as high as 0.35 $\mu\text{g/g}$). The highest concentration of Hg in streambed sediment (0.45 $\mu\text{g/g}$) was measured in a sample collected from Cache Creek (site 18) downstream of past Hg mining operations. No other streambed sites that drain the Coast Ranges had comparable Hg concentrations as the Cache Creek site because that is the only sampled site, within that physiographic province, downstream of geological deposits containing elevated Hg. Although the Hg measured in the streambed sediments of sites downstream of the Sierra Nevada can be partially attributable to mining, those Hg concentrations are decreasing in recent times because reservoirs constructed since 1968 in the lower Sierra Nevada trap some of the Hg transported from Au mining activities. Previous studies (e.g. Slotton et al., 1997) have shown that the reservoirs constructed in the lower Sierra Nevada and downstream of the Au mining region tend to act as sinks for Hg. Therefore, most of the Hg measured in streambed sediment of Sierran rivers was probably transported prior to the construction of the reservoirs.

The January 1997 flood discharge of some streams, especially at locations within or downstream of the Sierra Nevada, were among the highest ever recorded. At some locations, such as site 3 on the Sacramento River (Fig. 2) Hg in sediment concentrations dropped from 0.16 to 0.08 $\mu\text{g/g}$ following the flood. This was the case for the upper Sacramento River site (Fig. 2, site 3). A drop in Hg concentration by about one half was also measured for site 22 (Fig. 2) on the Sacramento River. At other locations, the difference was only minor. Mercury in sediment was higher by a factor of 3 in 1997 at the Cache Creek site increasing from 0.15 to 0.45 $\mu\text{g/g}$ (site 18). Because that site is downstream of Hg mining activities, it would be expected that variations in concentration would be apparent from year to year. Although the flood of 1997 probably moved large loads of Hg associated with sediment to downstream locations, that hydrologic event apparently had only minor effects on the concentrations of Hg in streambed sediment at most sites.

Most of the Hg in streambed sediment was measured as total Hg. At 5 sites, a final sampling of CH_3Hg^+ was

completed during the summer of 1998. That sampling was part of a pilot study (Krabbenhoft et al., 1999), conducted by the US Geological Survey, where samples for CH_3Hg^+ analysis were collected at numerous locations throughout the United States to determine the variation in CH_3Hg^+ concentrations nationwide and how those concentrations are related to geological or ecological characteristics and land use. The sites chosen (see Table 1 for site names) for that sampling included 2 agricultural sites (sites 20 and 21), a site on Putah Creek (site 23) downstream of Hg mining, 1 site on Bear River (site 15) downstream of Au mining activities, and 1 site on Cottonwood Creek (site 2) of mixed land use and natural mineralization. Methylmercury in streambed sediment concentrations ranged from a low of 0.27 ng/g at the Putah Creek site to a high of 2.84 ng/g at 1 of the agricultural sites — Sacramento Slough near Knights Landing site. Concentrations at the other 3 sites were 0.36 ng/g at the Cottonwood Creek site, 0.52 ng/g at the Colusa Basin Drain near Knights Landing site, and 0.55 ng/g at the Bear River site. The Sacramento Slough site also had the highest ratio (0.022) of CH_3Hg^+ to total Hg in sediment. The higher concentrations of CH_3Hg^+ in streambed sediment and ratio of CH_3Hg^+ to total Hg at the Sacramento Slough site can probably be attributed to hydrological factors, especially wetland density. Water in the Sacramento Slough is normally constrained within a channel for most of the year. However, the Sacramento Slough is flooded during wet years with runoff from the Sacramento Valley and from Sierra Nevada streams. The area surrounding the Sacramento Slough can remain flooded as much as 3 months of the year with runoff-induced water. Part of the land use upstream of the Sacramento Slough near Knights Landing sampling site is rice production, which involves the creation of temporary wetlands during the spring through late summer growing season. Water is periodically drained from the rice fields to the Sacramento Slough and the Colusa Basin Drain throughout the growing season. Therefore, the Sacramento Slough is more like a wetland throughout the year relative to most of the other sampling sites. It has previously been reported that CH_3Hg^+ production is related to the percentage of land cover that is wetland (Zilloux et al., 1993; St. Louis et al., 1994; Hurley et al., 1995). These sluggish water environments are ideal for Hg methylation because of longer water residence times, anoxic conditions in sediments, and availability of organic material for microbial processes. The higher levels of CH_3Hg^+ in streambed sediment at the Sacramento Slough site are probably related to the flooding and wetland-like characteristics of that site. Although the streambed sediments of Sacramento Slough have lower total Hg than a site such as Bear River at Highway 70 near Rio Oso (Fig. 2), the methylation efficiency appears to be much higher as indicated by the ratio of CH_3Hg^+ to total Hg at the Sacramento Slough (0.022) to the Bear River (0.003).

5.2. Mercury and methylmercury in unfiltered water

Mercury was measured in unfiltered water samples because most Hg is attached to particles of suspended sediment (Horowitz, 1995), or possibly present as fine particles of cinnabar or as elemental Hg, and, therefore, much of the mass transport is associated with the sediment particles. In addition, present water quality objectives for Hg, with respect to the protection of aquatic health, are written for concentrations in unfiltered water (Marshack, 1995). Methylmercury was also only measured in unfiltered water samples.

Boxplots for Hg in unfiltered water are shown in Fig. 3. The two sites with the highest concentrations are the Cache Creek site (site 17) and the Yolo Bypass site

(site 27). It was expected that the highest concentrations would be detected at these 2 sites because of the presence of Hg mines upstream in the Cache Creek Basin and because the Yolo Bypass carries stormwater runoff from the entire Sacramento River Basin. The highest Hg concentration was measured for the Cache Creek site, 2,248 ng/l. Both Hg and suspended sediment concentrations are highest in response to winter storm-water runoff. Suspended sediment and Hg concentrations are lower during late spring to fall because there is little rainfall and less suspended sediment transport. Sediment and Hg concentrations aggregated for all 12 sites are shown in Fig. 4. A second order equation can be fitted to the data with a resulting coefficient of determination (r^2) of 0.96. Previous studies (e.g. Mastrine et al.,

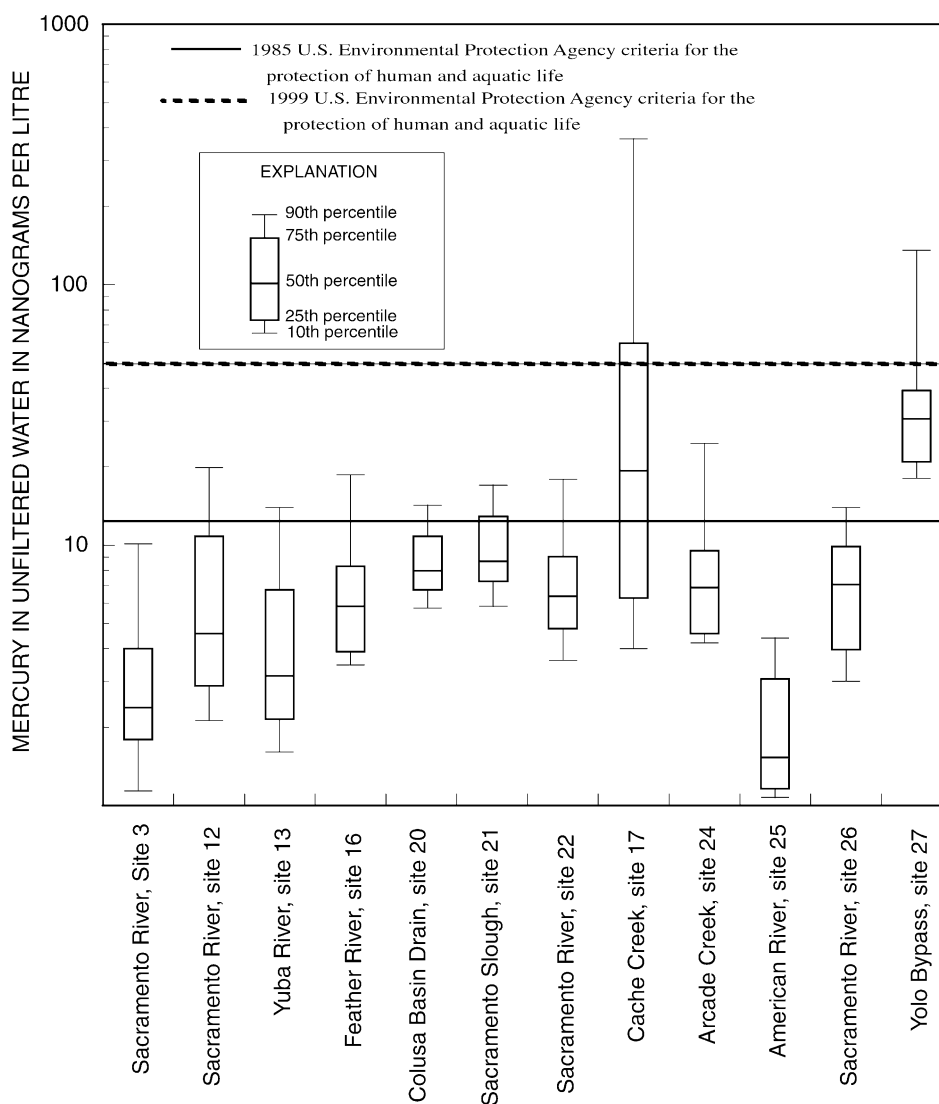


Fig. 3. Boxplots of Hg in unfiltered water. 1985 Hg criterion (Marshack, 1995), 1999 Hg criterion (US EPA, 1999).

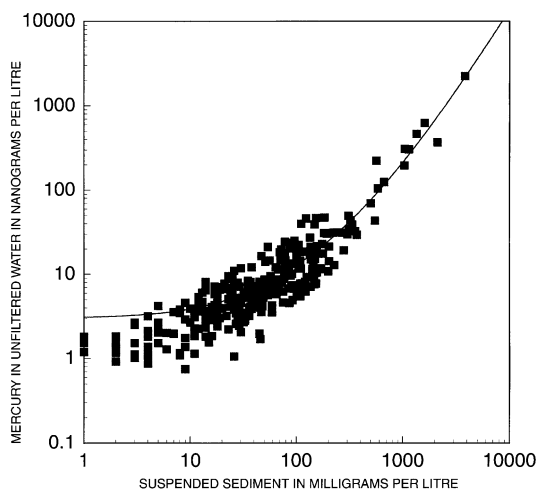


Fig. 4. Concentrations of Hg in unfiltered water and suspended sediment at all river sampling sites.

1999) have shown a linear correlation between Hg in unfiltered water and suspended sediment concentrations in precious metals mining areas. The Hg in water concentrations measured by Mastrine et al. (1999) were collected in the southeastern United States, with lower total Hg concentrations than those measured in the present study.

The lowest concentrations of Hg in unfiltered water were measured at the upper Sacramento River site (Fig. 3, site 3) and the American River site (site 25). The low Hg concentrations for the American River can be attributed to the upstream reservoir that probably traps most of the Sierran sediment and its associated Hg load. It was expected that rivers, such as the Feather River, draining the Sierra Nevada would contribute the greatest loading of Hg to the mainstem of the Sacramento River because of the source of Hg from abandoned Au mining. However, higher concentrations were measured at the mid-Sacramento River site (site 12) relative to the Feather River site (site 16), even though the mid-Sacramento River site is above the confluence of the Sacramento and Feather rivers. During the January 1997 flood, higher loadings of Hg in unfiltered water were transported from the part of the Sacramento River above the confluence with the Feather River relative to just below the confluence. It was concluded that an unknown source of Hg must be present upstream from the confluence of the Sacramento and Feather rivers. That source may be anthropogenic, but may also be related to geologic features, such as hot springs associated with volcanic deposits within the Cascade Range (Fig. 1). More recent samples taken in January and February 2000, under stormwater runoff conditions, have demonstrated that one stream (Mill Creek, site 28, Fig. 1) draining the Lassen volcanic area does in fact contain elevated levels of total Hg and CH_3Hg^+ (max-

imum measured concentrations of 100 and 0.5 ng/l respectively).

The recommended water-quality criterion for total Hg in water was originally recommended in 1985 by the US EPA. The recommended criterion for protection of human and aquatic health was set at 12 ng/l for freshwater systems (Marshack, 1995). The recommended criterion was revised in 1999 to 50 ng/l for freshwater aquatic systems (US EPA, 1999). Concentrations above either the 1985 or 1999 criteria are most likely to occur during the winter months because during that time most of the precipitation occurs resulting in high river flows. During this study, the 12 ng/l criterion was exceeded for as much as 5 consecutive months at the mid-Sacramento River site (site 12). The highest measured Hg concentrations on the Sacramento River, 105 ng/l, were in samples collected at site 12 during the flood of January 1997. That site also had the highest Hg concentrations, 43.5 ng/l, of any site on the mainstem Sacramento River, measured during the winter of 1997–1998. The 1999 criterion of 50 ng/l was not exceeded as frequently. Only the Cache Creek at Rumsey and the Yolo Bypass at Interstate 80 near West Sacramento had concentrations above the 1999 criterion.

Samples were collected for the analysis of reactive Hg at the same 12 sites as the ones collected for Hg in unfiltered water. The purpose of the reactive Hg sampling is to determine what portion of the transported Hg is reactive to a strong reducing agent such as SnCl_2 . That reaction provides some insight as to the relative potential for the transported Hg to undergo geochemical or possibly biogeochemical transformations in the environment. In general, the amount of reactive Hg at any site was low, less than 8% of the total Hg at all sites, indicating that very little of the transported Hg in this basin is present as the free ion or in a form that can be easily reduced to elemental Hg (Fig. 5). The Cache Creek site had very little reactive Hg present during high water sampling. The sample collected at Cache Creek had the highest single concentration of total Hg in unfiltered water of any sample collected in this study, 2,248 ng/l. The reactive portion of that Hg was 0.0024 ng/l. During storm-water transport, most of the Hg transported in the water column at Cache Creek is probably cinnabar. Because of the weak solubility of that mineral, very little can be reduced by SnCl_2 . The site with the highest proportion of reactive Hg, 7.8% of the total, was the Sacramento Slough site (site 21). The Sacramento Slough was under flooded conditions, with floodwater transported from various locations, at the time of the high-water sampling, resulting in sluggish water flow and slow drainage through the region and longer water residence time. The Sacramento Slough site is more like a wetland under those conditions. The higher amount of reactive Hg at that site is probably related to these flooded conditions.

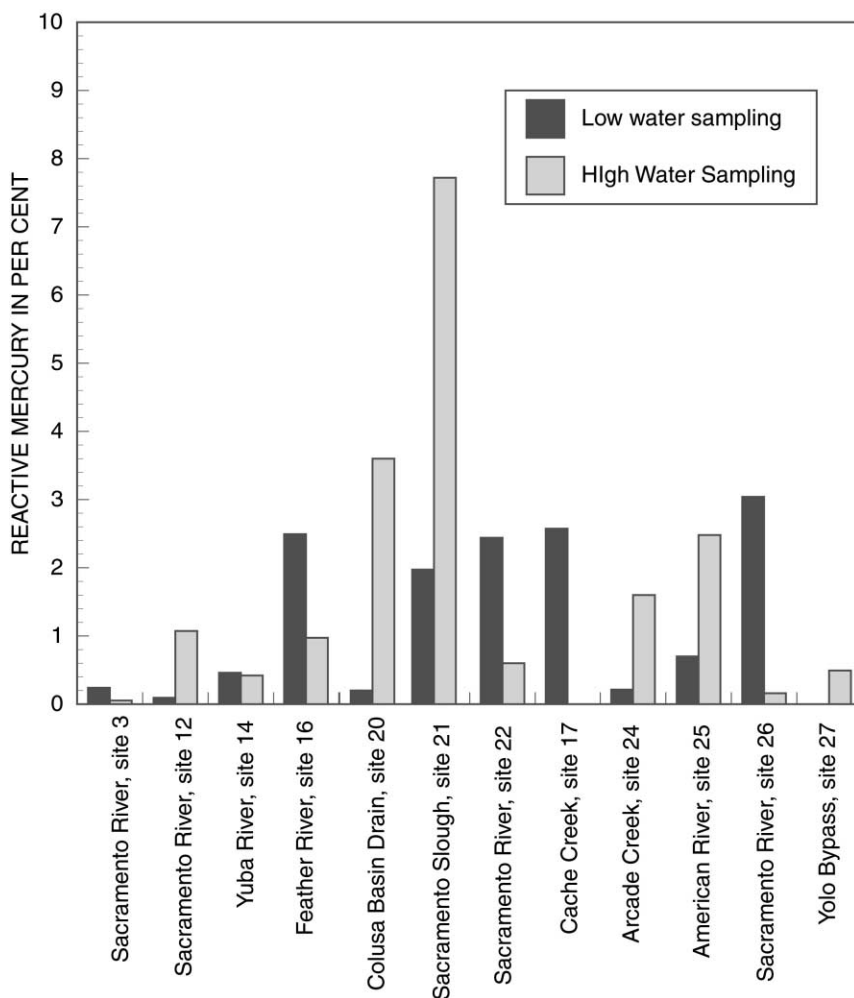


Fig. 5. Reactive Hg in per cent at all river sampling sites.

Boxplots of CH_3Hg^+ in unfiltered water for the 5 sites in this study are shown in Fig. 6. The highest median concentration of CH_3Hg^+ (0.191 ng/l) was for the Colusa Basin Drain site (site 20). As expected, because it is located upstream of most agricultural drainage, the mid-Sacramento River site (site 12) had the lowest median CH_3Hg^+ (0.102 ng/l). There is no water quality standard in the United States for CH_3Hg^+ . However, a concentration ≤ 0.1 ng/l of CH_3Hg^+ has been suggested as being representative of pristine water (Rudd, 1995). The US EPA (2001) has recently suggested national bioaccumulation factors (BAFs) for CH_3Hg^+ designed to limit the accumulation of CH_3Hg^+ in fish tissue of various trophic levels to levels below 0.3 mg/kg of tissue. The 0.3 mg/kg level is for protection of human health with respect to fish consumption (US EPA, 2001). For upper level trophic fish, the BAF corresponding to 0.3 mg/kg of CH_3Hg^+ in fish tissue translates to a dissolved CH_3Hg^+ concentration of 0.11

ng/l. Further work needs to be completed to define the actual CH_3Hg^+ BAF values for this major river system. The median CH_3Hg^+ concentrations for the Sacramento River sites are close to 0.1 ng/l (Fig. 6). The median concentrations of the two agricultural sites were greater than 0.1 ng/l. The median concentration for the Sacramento Slough site (site 21) was 0.152 ng/l, and that for the Colusa Basin Drain site (site 20) was 0.191 ng/l. Although the highest median concentration was recorded for the Colusa Basin Drain, that median is statistically different only from the lower Sacramento site (site 26) ($P=0.036$) according to the Mann–Whitney nonparametric test.

For the two agricultural sites, it was expected that higher concentrations of CH_3Hg^+ would be measured at the Colusa Basin Drain site (site 20), relative to the Sacramento Slough site (site 21), because of differences in water chemistry. Higher concentrations of SO_4^{2-} (median concentration = 66 mg/l) are measured at the Colusa Basin Drain site and the conversion of inorganic

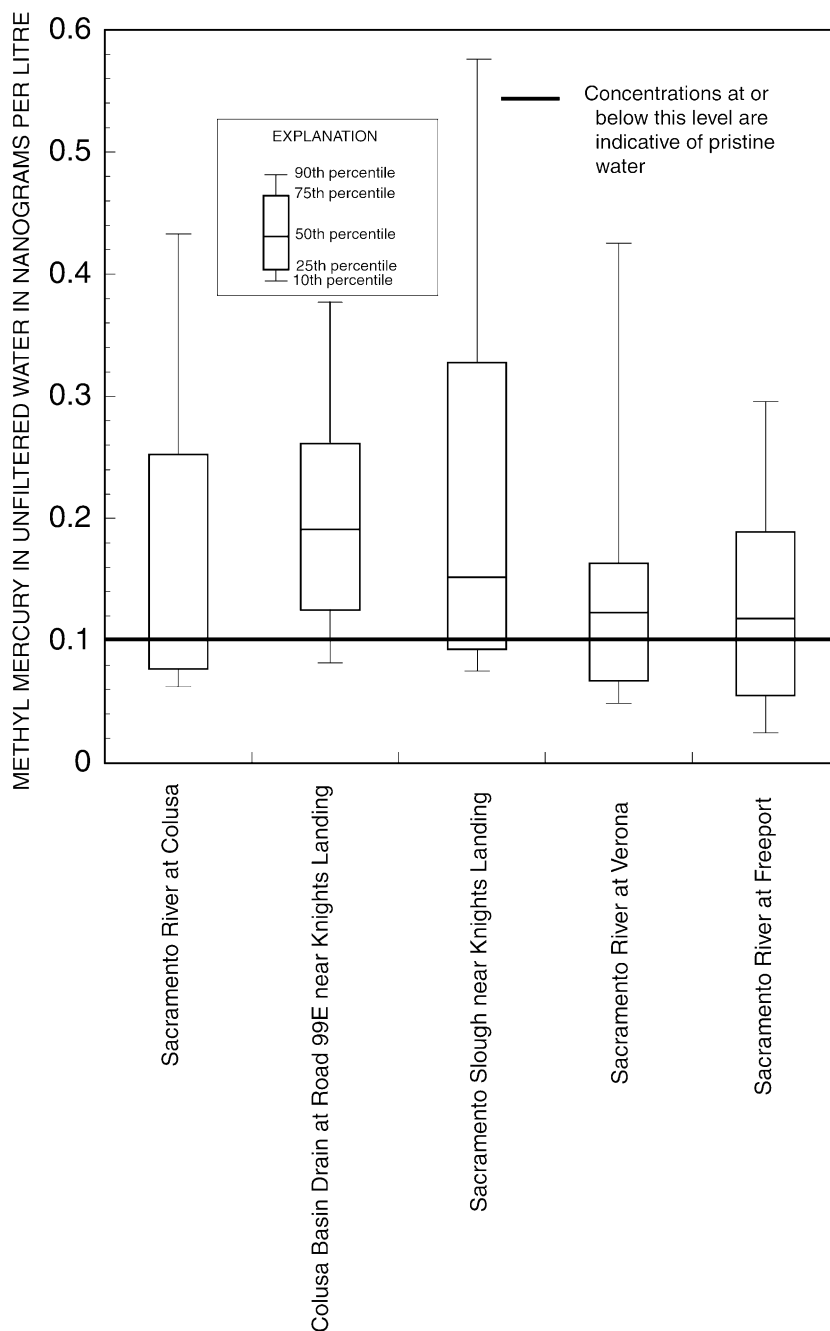


Fig. 6. Boxplots of CH_3Hg^+ at select river sampling sites.

Hg to CH_3Hg^+ is thought to be linked to SO_4^{2-} reducing bacteria (Zilloux et al., 1993). The median SO_4^{2-} concentration at the Sacramento Slough site (site 21) was 9 mg/l, and that of the nearest site on the Sacramento River (site 22) was 5.3 mg/l. Although the median concentration of CH_3Hg^+ at the Colusa Basin Drain is slightly higher than that of the Sacramento Slough site (site 21), the difference is not statistically

significant when tested by the Mann–Whitney nonparametric test of medians. Therefore, environmental factors other than SO_4^{2-} concentrations, such as wetland density, may be responsible for the slightly higher CH_3Hg^+ concentrations in water and sediment of the Sacramento Slough site (site 21).

There is a seasonal component to CH_3Hg^+ concentrations measured for this study (Fig. 7). The lowest

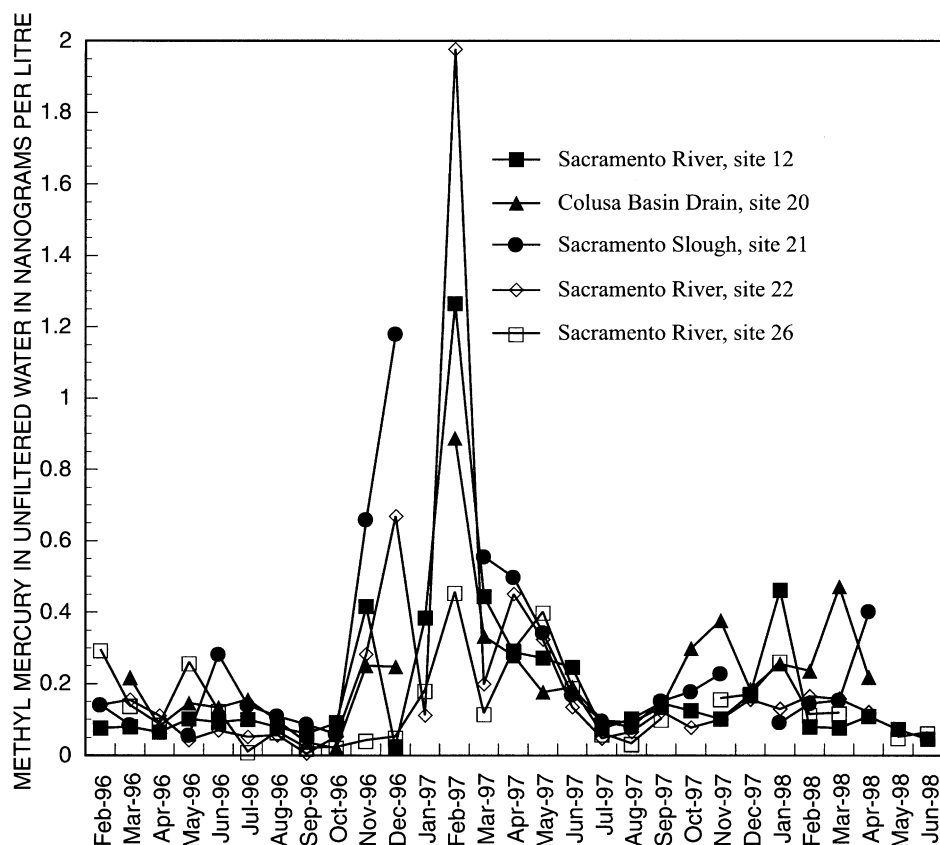


Fig. 7. Time series plot of CH_3Hg^+ at select river sampling sites.

concentrations are measured during middle to late summer. Higher concentrations tend to be measured during the fall to winter months. The highest concentrations for the period of this study were measured during January and February 1997. The high CH_3Hg^+ concentrations measured in January and February 1997 at these sites can be attributed to the January 1997 flood. During the winter of 1997–1998, higher than normal amounts of rain were recorded for much of the Sacramento River Basin. Although higher than normal amounts of rainfall were recorded, there was no single storm of the magnitude of the January 1997 flood. Therefore, CH_3Hg^+ concentrations increased during the 1997–1998 winter, but not to the extent of the previous year. The impact of these CH_3Hg^+ concentrations and the implication to downstream water bodies, such as the San Francisco Bay, has yet to be determined.

Attempts to correlate CH_3Hg^+ with other water quality parameters such as suspended sediment and dissolved organic C were unsuccessful (Fig. 8). This suggests that most of the CH_3Hg^+ must be transported independently of either the dissolved organic C or the suspended sediment. No statistically significant correlation of CH_3Hg^+ with either dissolved organic C or suspended

sediment was noted in this study for either individual sites or when data were aggregated for all sites. This is in contrast to the correlation of total Hg with suspended sediment (Fig. 4).

Mercury in the Sacramento River is transported to a major receiving body of water, the estuary system of the San Francisco Bay, where transformations, such as methylation or demethylation and bioaccumulation, are possible within the estuarine wetland environments. The amount of Hg transported for 3 winters (20 December–20 March) was calculated by determining the load of total Hg at the Yolo Bypass site (Table 1, site 27) and the downstream Sacramento River site (site 26). The total amount of Hg transported out of the Sacramento River Basin during the winter of 1996–1997 was calculated to be 487 kg; most of that was associated with the flooding, as reported previously (Domagalski, 1998). That study also demonstrated that approximately 75% of the Hg load was attributable to the reach between sites 3 and 12 (Table 1) with the remaining load contributed from other sources including Cache Creek. That reach of the Sacramento River between sites 3 and 12 is above the confluence of the Sacramento and Feather rivers, and, therefore, the streams draining the

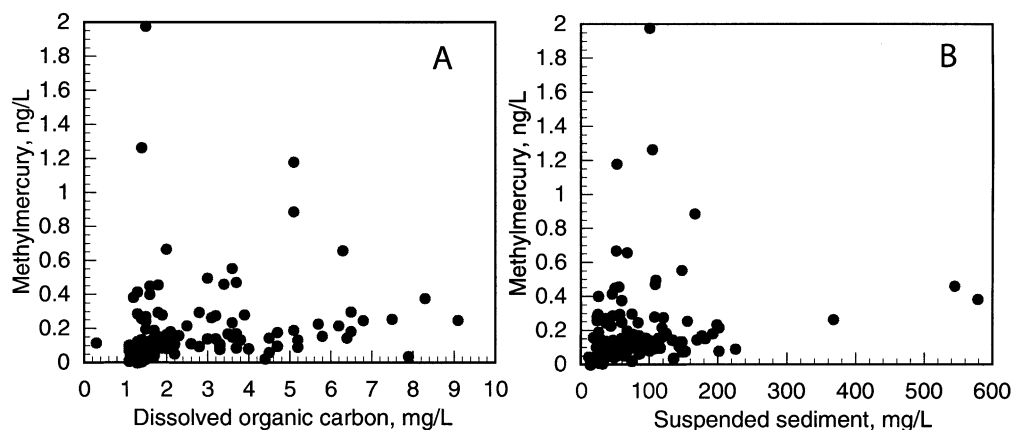


Fig. 8. (A) Plot of CH_3Hg^+ and dissolved organic carbon; (B) plot of CH_3Hg^+ and suspended sediment.

Au mining region were not the principal source of Hg in spite of the high precipitation over the Au mining region. During the winter of 1997–1998 precipitation amounts were high throughout much of the Sacramento River Basin. The Yolo Bypass was used as a flood control channel for a longer time period. The total amount of Hg transported out of the Sacramento River Basin during the 1997–1998 winter was calculated to be 506 kg. As for the case of the previous winter, most of the Hg load was transported through the Yolo Bypass. The winter of 1998–1999 was different from the previous two winters in that precipitation in the Sacramento Valley was lower than average, but precipitation in the Sierra Nevada was higher than average. Because of the lower than normal amounts of precipitation in the valley, the Yolo Bypass was not needed as much for flood control purposes as in the previous two winters and, as a result, much less water was transported out of the basin through the bypass. The total amount of Hg transported out of the basin during the winter of 1998–1999 was calculated to be 169 kg. Previous work by Foe and Croyle (1998) has shown that the amount of Hg transported out of the Sacramento River Basin can be as high as 800 kg/a. That calculation was made in the time frame from 1 May 1994 to 30 April 1995, with most of the mass (98%) transported during the winter rainy season.

The mass of CH_3Hg^+ transported out of the Sacramento River Basin could not be calculated because only a relatively few samples were collected at the Yolo Bypass and, therefore, the variability in concentrations at that site is unknown. Instantaneous CH_3Hg^+ loads could be calculated for the site on the Sacramento River (Table 1, site 22), which is just downstream of the confluence with the Feather River and downstream of the agricultural tributaries. That site would potentially have some of the highest CH_3Hg^+ concentrations of any Sacramento River site and would be representative, during the winter season, of CH_3Hg^+ contributions to

the Yolo Bypass from the Sacramento River. Methylmercury loads in the Sacramento River at site 22 are lowest during the late spring through fall season. Methylmercury loads range from nearly 10 to <1 g/d. The highest loadings occurred during the winter of 1996–1997. The greatest load during that period was 282 g/d calculated for a sample collected during February 1997. The load decreased to 8 g/d in March in response to lower amounts of rainfall. Methylmercury loadings were more consistent in the subsequent winter of 1997–1998. Methylmercury loads increased from 8 g/d in December 1997 to 20 g/d in January, and remained at levels of 28 and 24 g/d in February and March, respectively. Loads decreased to 10 g/d in April. Further work is necessary to determine the actual loads of CH_3Hg^+ transported from the Yolo Bypass and to determine how the contribution of CH_3Hg^+ to the San Francisco Bay Estuary from the Sacramento River Basin compares to the amount produced within the estuary system.

6. Summary and conclusions

Mercury concentrations and transport in rivers of the Sacramento River Basin are elevated because of geological deposits, mining of Hg, and the use of Hg in historic Au mining operations. Mercury accumulation in fish has resulted in advisories against consumption for certain species both in the Sacramento River and downstream within the estuary system of the San Francisco Bay. In addition, current plans to restore wetlands in the San Francisco Bay system may result in increased rates of Hg methylation as sites with Hg contaminated soil may be permanently inundated with water. Prioritization of the remediation of mining sites requires knowledge of the forms of Hg and the potential for methylation or bioaccumulation. The Cache Creek was found to have some of the highest concentrations of total Hg of all

streams of this study. Because of the type of Hg (cinnabar) found naturally in that basin, the reactivity of the Hg, within Cache Creek, was low during times of high Hg transport. That reactivity may change after transport of the Hg-laden particulate matter to the San Francisco Bay. An uncharacterized source or sources of Hg to the Sacramento River was determined to be located somewhere between sites 3 and 12. Those sources contributed a greater load of Hg to the Sacramento River during stormwater runoff conditions relative to the Feather River, the stream that would carry Hg from the Au mining region. Recent sampling has shown that at least 1 of these sources is Mill Creek, which drains a volcanic region. The load of Hg from that source is naturally occurring. Methylmercury concentrations in water were dependent on hydrological conditions. Lowest concentrations tended to be measured during late summer or early fall — a time of low streamflow. Although CH_3Hg^+ concentrations in river water were elevated during a year of prolonged rainfall, the highest concentrations were measured in association with an extreme event in the winter of 1997. Most of the Hg in unfiltered water was unreactive when assessed through the reactive Hg test where a strong reducing agent was added to the water. The site with the highest amount of reactive Hg, 7.8% of the total Hg in water, was the Sacramento Slough. That site also had the highest amount of CH_3Hg^+ in sediment. The author suggests that the factor most responsible for the higher amounts of reactive Hg and CH_3Hg^+ at the Sacramento Slough was the greater amount of wetland land cover at that sampling site.

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